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Chelated Borates: Synthesis, Reactivity, and Cation Formation

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The ligands *N*-salicylidene-*o*-aminophenol (LH$_2$), *N*-(5-chlorosalicylidene)-*o*-aminophenol (L(Cl)H$_2$), and *N*-(5-bromosalicylidene)-*o*-aminophenol (L(Br)H$_2$) were used to prepare a series of borates having the formulas LBOR (R = Me (**1**), Et (**2**), ^{n}Pr (**3**), ^{n}Bu (**4**)), L(Cl)BOR (R = Me (**5**), Et (**6**), ^{n}Pr (**7**), ^{n}Bu (**8**)), and L(Br)BOR (R = Me (**9**), Et (**10**), ^{n}Pr (**11**), ^{n}Bu (**12**)). Either **1**−**4** or **9**−**12** could be combined with HOSiPh$_3$, to form unique compounds possessing a single B−O−Si linkage, LBOSiPh$_3$ (**13**) and L(Br)BOSiPh$_3$ (**14**), respectively. The charged species, [LB(thf)]$^+$OTf$^-$ (**15**) forms when **1** is combined with HOTf. It can be used as a catalyst for the oligomerization of propylene oxide. By comparison, [^{n}Bu$_2$B]$^+$OTf$^-$ effects the oligomerization to the same extent as **15**, but the neutral species, **1**−**4**, **13**, and **14** do not, even under forcing conditions. All of the compounds were characterized by melting point, ^{1}H NMR, IR, elemental analyses, and, in the case of **13**, by X-ray crystallography.

Introduction

In recent years there has been an explosion of interest in the development of group 13 Lewis acid catalysts.[1] These have generally consisted of neutral compounds having an open coordination site that is, in some cases, intramolecularly protected. This is true, for example, in the methylaluminum bis(phenoxide) suite of catalysts for activating aldehydes.[2] Incorporating chirality into the Lewis acid catalyst is particularly effective.[3] Cationic group 13 derivatives may be expected to have enhanced Lewis acidity by comparison to the neutral derivatives. With aluminum this also means that the reagents can be used in less air-sensitive conditions, a situation that limits the more readily available neutral derivatives. Moreover, it is not always necessary to go through the arduous process of designing an unsaturated system. Cations can either be supported by solvent molecules (as in the [SalenAl(solvent)$_2$]$^+$X$^-$ systems)[4] or can exist in an equilibrium in which the cation predominates during the reaction under consideration. An example of this latter type is a chiral oxazaborinane complex which has been described as a "super" Lewis acidic catalyst.[5] A wide range of cationic boron compounds, primarily with nitrogen supporting groups, has been reported (called "borenium" for the three-coordinate and "borinium" for the two-coordinate varieties).[6] However, the applicability of boron cations in catalysis has only begun to be explored.

The present work will explore the use of boron cations in the polymerization of propylene oxide (PO). It has previously been shown that PO can be polymerized by aluminum cations.[4] Thus, a comparison between the use of aluminum and boron in this application will be possible. The cations are derived from chelated borates of the form LBOR (where L = a tridentate (−O$_2$N) ligand and R = Me, Et, ^{n}Pr, and ^{n}Bu). The presence of an −OR group on boron in the place of the commonly employed −R or −Ar makes these compounds of great utility in further reactions. For instance, they can be used to prepare the derivatives LBOSiPh$_3$, a unique class of molecules containing a single B−O−Si linkage.

Results and Discussion

Neutral Borates. Heavier group 13 compounds (Al, Ga, and In) often derive from alkyl reagents. In combination with protic reagents, such as a phenol, at least 1 mol of alkane is readily eliminated in forming the compound. This reaction pathway is not readily available for boron; alkylboron compounds are generally stable in the presence of protic reagents.[7] This reactivity difference can be attributed to the fact that the B−C bond is not polar when compared to the M−C bond (with M = Al, Ga, In). The B−O bond, however, is polar and readily protonated. Thus, the most common synthetic routes for introducing a ligand on boron involve use of either a boronic acid (RB(OH)$_2$) or borate (B(OR)$_3$) (eqs 1 and 2, respectively; R = alkyl or aryl).[8] The boronic acid derivatives are generally very stable and do not undergo further reactions while a third

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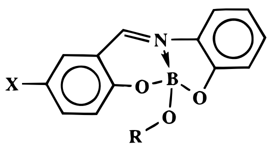


X	Ligand	R
H	LH_2	Me (**1**), Et (**2**), ^nPr (**3**), ^nBu (**4**)
Cl	$L(Cl)H_2$	Me (**5**), Et (**6**), ^nPr (**7**), ^nBu (**8**)
Br	$L(Br)H_2$	Me (**9**), Et (**10**), ^nPr (**11**), ^nBu (**12**)

Figure 1. General structure and numbering of borates **1**−**12**.

alcohol elimination can be utilized from the borate derivatives.

$$LH_2 + RB(OH)_2 \rightarrow LBR + 2H_2O \qquad (1)$$

$$LH_2 + B(OR)_3 \rightarrow LBOR + 2HOR \qquad (2)$$

This latter reaction can be used to prepare the comprehensive series of compounds **1**−**12** with three ligands and four R groups (Figure 1). These compounds are unique since most of the related derivatives contain alkyl or aryl groups on boron rather than an alkoxide.[9] There is little variability in the spectroscopic data throughout the series. For instance, the imine (HC═N) ^1H resonance falls in the narrow range of δ 8.47−8.55 ppm and the B−N IR absorption is found as a strong to moderate peak in the range 1004−1031 cm^{-1}. A four-coordinate geometry is also confirmed in the ^{11}B NMR of **1** (δ 4.26 ppm). By comparison $[Me_2B(NH_3)_2]^+$ and $[(PhBO)(Ph_2SiO)_2]$[10] demonstrate shifts of δ 13.9 and 28.2 ppm, respectively, and the three-coordinate derivative $Me_2B(OMe)$ demonstrates a shift of δ 53 ppm.[11] The compounds are moisture sensitive and produce ligand (LH_2) and an unidentified boron-containing species when hydrolyzed. By comparison, the hydrolysis of chelated boron compounds, such as LBPh (where L = various aliphatic diols), produces $PhB(OH)_2$ in high yields.[12]

Compounds **1**−**12** should be structurally similar to those incorporating an $-O_2N$ ligand (Figure 2a[13] and b[14]) and other related derivatives (Figure 2c[15] and d[16]). Some structurally characterized examples demonstrate the unassociated, monomeric nature of the molecules. This is observed, for example, in *B*-phenyl[amino-2,2′-diethylene-*O,O,′N*] borane[13] and *B*-phenyl[amino-2,2′-diphenolate-*O,O,′N*] borane.[14] A low-quality structure for **2** supports this formulation (Figure 3).[17] In the structure the boron atom is in a four-coordinate, tetrahedral geometry. By comparison, aluminum can form bimetallic, $[(H_2O)LAl(\mu\text{-}MeCO_2)(\mu\text{-}OH)AlL(H_2O)]$, and highly aggregated, $[\{LAl(H_2O)(OH)_2\}_2Al(\mu\text{-}OH)_2Al\{LAl(H_2O)(OH)_2\}_2]$, complexes with the LH_2 ligand.[18]

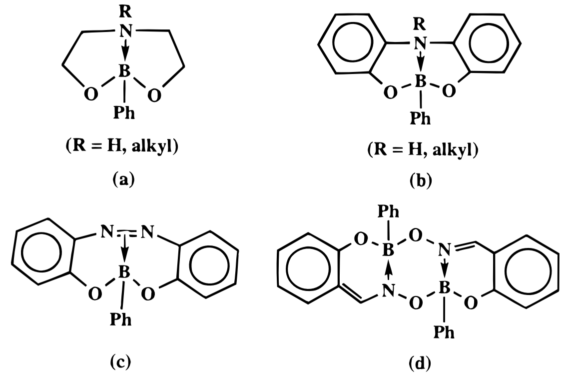


Figure 2. General depiction of derivatives related to **1**−**12**.

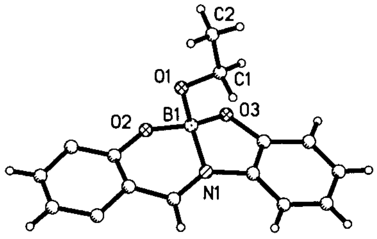
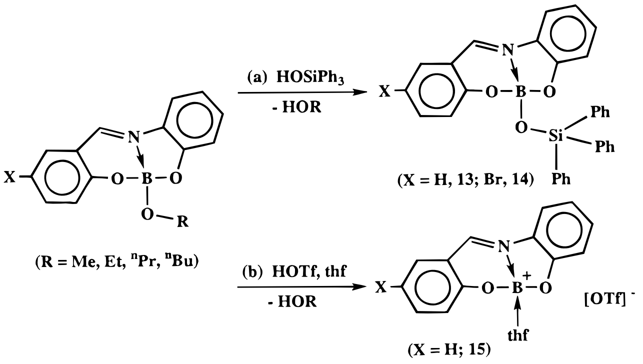


Figure 3. Computer-aided drawing of compound **2**.

Scheme 1. Borate Reactions To Form Siloxides (a) and a Boron Cation (b)



Borate Reactivity. Any of the borates (**1**−**4** and **9**−**12**) can be combined with $HOSiPh_3$ to form the siloxide derivatives **13** and **14** (Scheme 1a). The ^1H NMR spectra for these compounds are similar to those observed for **1**−**12**; the HC═N resonances appear at δ 8.12 and 8.07 ppm, and the B−N absorbance occurs at 1031 and 1028 cm^{-1}. Furthermore, the ^{11}B spectrum of **13** consists of one resonance at δ 2.77 ppm. The compounds are moisture sensitive and form free ligand (LH_2) and an uncharacterized boron compound when hydrolyzed.

An X-ray structure confirms the tetrahedral geometry around boron for **13** (Figure 4 and Tables 1 and 2). The most acute angle is found for the five-membered ring (O(1)−B(1)−N(1), 98.6(5)°), while the six-membered ring demonstrates a near ideal angle (O(2)−B(1)−N(1), 109.4(5)°). The B−O bond distance is consequently longer for the five-membered ring (1.465(7) Å) than for the six-membered ring (1.433(7) Å). The B−N distance is longer still (1.599(8) Å). However, this distance is shorter than those observed for the related systems derived from the ligands shown in Figure 2a (LBPh, 1.661(3) Å)[13] and 2b

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[17] Only a computer-generated view will be provided here. X-ray data: monoclinic, $P2_1/c$, $a = 26.381(3)$ Å, $b = 7.3169(9)$ Å, $c = 14.236(2)$ Å, $\beta = 105.604(3)°$, $V = 2648.8(1)$ Å^3, $R_1 = 17.55\%$ for 1114 data having $F_o > 4\sigma(F)$.

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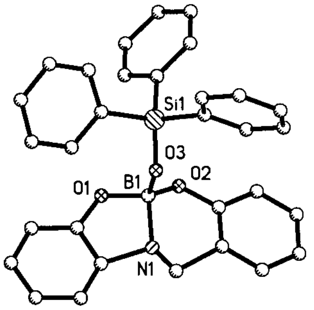

Figure 4. Molecular structure and atom-numbering scheme for **13**.

Table 1. Data Collection and Processing Parameters for Complex **13**

formula	$C_{31}H_{24}NO_3BSi$
fw	497.41
color, habit	yellow prism
cryst size (mm^3)	0.5 × 0.3 × 0.2
cryst system	triclinic
space group	$P\bar{1}$
a (Å)	9.481(1)
b (Å)	10.762(1)
c (Å)	14.395(1)
α (deg)	71.16(1)
β (deg)	78.48(1)
γ (deg)	67.62(1)
V (Å^3)	1280.6(2)
Z	2
D(calcd) (g cm^{-3})	1.290
μ (mm^{-1})	0.126
$2\theta_{\max}$ (deg)	45
unique data measd	3917
obsd data	2327 [$F \geq 4\sigma(F)$]
no. of variables	334
S (GOF)	1.04
R1 (%)[a]	5.7
R_w (%)	11.6

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **13**

Si(1)−O(3)	1.616(3)	Si(1)−C(20)	1.857(5)
Si(1)−C(14)	1.863(4)	Si(1)−C(26)	1.868(5)
B(1)−O(3)	1.404(6)	B(1)−O(2)	1.433(7)
B(1)−O(1)	1.465(7)	B(1)−N(1)	1.599(8)
O(3)−Si(1)−C(20)	112.0(2)	O(3)−Si(1)−C(14)	108.8(2)
C(20)−Si(1)−C(14)	108.6(2)	O(3)−Si(1)−C(26)	106.3(2)
C(20)−Si(1)−C(26)	110.6(2)	C(14)−Si(1)−C(26)	110.6(2)
O(3)−B(1)−O(2)	114.7(5)	O(3)−B(1)−O(1)	113.4(5)
O(2)−B(1)−O(1)	112.9(4)	O(3)−B(1)−N(1)	106.4(4)
O(2)−B(1)−N(1)	109.4(5)	O(1)−B(1)−N(1)	98.6(5)
C(1)−O(1)−B(1)	111.9(4)	C(9)−O(2)−B(1)	113.2(4)
B(1)−O(3)−Si(1)	142.8(3)		

(LBPh, 1.699(5) Å)[14] as well as in bidentate chelates such as those derived from ethanolamine (LBR$_2$; R = Ph, 1.657(3) Å; *p*-tolyl, 1.655(2) Å).[19]

This would appear to be the first compound to contain a single, terminal B−O−Si linkage. Other compounds containing this unit are generally cyclic. As examples consider the six-membered systems PhB(OSiMe$_2$)$_2$X (where X = O and NMe)[20] and [(PhBO)(Ph$_2$SiO)$_2$O][10,21] and the eight-membered system [PhB(OSiPh$_2$)O]$_2$.[10,21] Despite the cyclic nature of these compounds, the latter two demonstrate similar B−O (1.374(7) and 1.347(2) Å, respectively) and O−Si distances (1.650(8) and 1.621(9) Å, respectively) to those of **13** (B−O, 1.404(6) Å; O−Si, 1.616(3) Å).

Most closely related to **13** and **14** are some derivatives of aluminum, SalenAlOSiPh$_3$, which were only recently reported.[22] By comparison to **13**, these feature either a square pyramidal or trigonal bipyramidal coordination around the central five-coordinate aluminum. The Al−O−Si angles are exceptionally wide (from 157.9(14) to 166.8(6) °). In **13** this angle reflects a lessened steric effect at a value of 142.8(3)°. However, this angle demonstrates just how wide an unassociated B−O−Si linkage can become.

Cation Formation. Strong acids such as HOTf (HOSO$_2$CF$_3$) and HOTs (*p*-toluenesulfonic acid) can be used to remove an alkyl or alkoxide from a suitable boron starting material. In the case of **1**−**4** combination with HOTf leads to the cation−anion pair [LB(thf)]$^+$OTf$^-$ (Scheme 1b). The ^{11}B NMR shift of δ 3.91 ppm confirms the presence of thf and a four-coordinate geometry around the boron atom. The ^{1}H NMR and analyses provide further evidence for the presence of thf in the sample. While two-, three-, and four-coordinate cations are well-known,[24] there are none supported by a tridentate chelate. Compound **15** is the first. It is expected that the thf occupies a T_d coordination site like the −OSiPh$_3$ group in **13**.

Catalytic Activity. Compounds **1**, **13**, and **15** were examined for activity as propylene oxide (PO) polymerization catalysts under mild (25 °C, atmospheric pressure) and forcing conditions (40 °C and 8 psi pressure). The results indicated that only the cationic boron complex produced polymer under any condition. The polypropylene oxide (PPO) had similar values for reactions both at ambient temperature (M_n, 416; M_w, 607; PDI, 1.46) and under moderately high temperatures and pressures (M_n, 414; M_w, 624; PDI, 1.51). This indicates that the boron cation was only marginally effective in polymerizing PO.

Commercial [^{n}Bu$_2$B]$^+$OTf$^-$ (**16**) is a well-known Lewis acid reagent and has been used in the preparation of vinyloxyboranes[23] and borylazaenolates[24] and as a macrolactonization catalyst.[25] It is better than **15** in the polymerization of PO (M_n, 808; M_w, 1299; PDI, 1.61). By comparison, the aluminum cations [SalenAl(MeOH)$_2$]$^+$[BPh$_4$]$^-$ performed in a manner intermediate between **15** and **16** (for L = Salen, Salen(Cl), and Acen the average was the following: M_n, 422; M_w, 633; PDI, 1.50). This is despite the fact that they were run in the presence of a protic reagent (usually used to quench living polymerizations) and for only 12 h. The mechanism proposed for the aluminum cation involved the use of a sixth coordination site.[4] Each incoming monomer was envisioned to be activated prior to insertion into the growing polymer (Figure 5a displays how the mechanism would appear for boron). However, a fifth coordination site is unreasonable to suggest for **15** and a fourth not known for **16**. On the basis of the different coordination numbers for **15** and **16**, it is most likely that the chain growth mechanism is one in which the polymer chain transfers to a new monomer that has become coordinated by the boron cation. The insertion can occur either through dissociation of the

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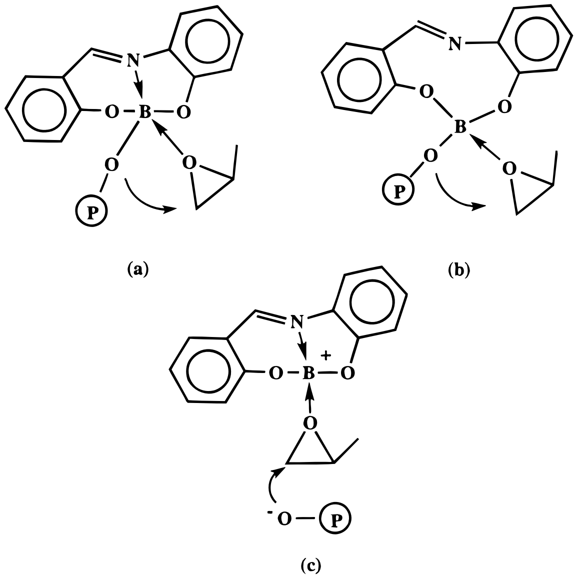

Figure 5. Potential mechanisms for the polymerization of propylene oxide.

transannular B−N bond to provide an open coordination site for the incoming monomer (Figure 5b) or through dissociation of the −O−Ⓟ chain (Figure 5c). Studies on bicyclic derivatives of the general formula B{O(CH$_2$)$_n$}$_3$N ($n = 2, 3$) indicate that the transannular B−N bond strength is about 56 kJ·mol^{-1}.[26] By any estimate the bond energy for a B−O linkage is much higher.[27] Thus, the interaction of PO with **15** and **16** should be viewed as an anionic polymerization[28] in which the incoming monomers are accommodated in an open coordination site provided by release of the B−N bond. They subsequently insert into the B−O−polymer linkage.

Conclusions

A complete series of new chelated borates (LBOR (R = Me, Et, ^{n}Pr, ^{n}Bu) is now available for general use. These can participate in a wider range of reactions than the more well-known alkyl derivatives (LBPh, for example). For instance they can be used to prepare novel compounds containing a single B−O−Si linkage (LBOSiPh$_3$) as well as prepare the cation/anion pair (LB(thf)$^+$OTf$^-$). As a new Lewis catalyst, this ion pair acts as a weak catalyst toward propylene oxide. More uses of these cations in Lewis acid catalysis are currently being sought.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glovebox. All solvents were rigorously dried prior to use. ^{1}H and ^{11}B NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 and 86.55 MHz, respectively, and are reported relative to SiMe$_4$ and in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer and were satisfactory for all compounds. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[29] B(OR)$_3$ reagents and [Bu$_2$B]$^+$OTF$^-$ were used as purchased from Aldrich. Propylene oxide was purchased from the same source and dried over CaH$_2$ prior to use. X-ray data for **2** and **13** were collected on a Siemens SMART-CCD unit. There were two molecules in the independent unit of **2**. There were problems with this structure so only only a preliminary description is given. Oligomeric polypropylene oxide (PPO) was characterized using gel permeation chromatography using a Waters 510 HPLC pump and 746 Data Module against polystyrene standards. Infrared data and elemental analyses are located in the Supporting Information. Compounds **1**−**12** were obtained as analytically pure pale yellow solids.

Synthesis of L[B(OMe)] (1). To a stirred toluene/thf (4:1) solution (25 mL) of H$_2$L (0.43 g, 2.01 mmol) was added trimethyl borate (0.209 g, 2.01 mmol). The resulting solution was refluxed for 4 h, and then the solvent was removed under vacuum to yield a pale yellow solid (0.40 g, 78%): Mp 203−204 °C; ^{1}HNMR (270 MHz, CDCl$_3$) δ 3.15 (s, 3H, OCH_3), 6.92 (m, 2H, Ph*H*), 7.12 (m, 2H, Ph*H*), 7.25 (m, 2H, Ph*H*), 7.56 (m, 2H, Ph*H*), 8.55 (s, 1H, NC*H*); ^{11}B NMR (270 MHz, CDCl$_3$, external standard BF$_3$·Et$_2$O) δ 4.26.

Synthesis of L[B(OEt)] (2). Procedure as for **1** with H$_2$L (0.43 g, 2.01 mmol) and triethyl borate (0.29 g, 2.01 mmol). After filtration and concentration, a pale yellow solid precipitated and a few needle crystals were grown at −30 °C (0.38 g, 70%): Mp 180−182 °C; ^{1}HNMR (270 MHz, CDCl$_3$) δ 1.00−1.03 (t, 3H, CH$_2$CH_3), 3.38−3.42 (m, 2H, OCH_2), 6.91 (m, 2H, Ph*H*), 7.11 (m, 2H, Ph*H*), 7.24 (m, 2H, Ph*H*), 7.55 (m, 2H, Ph*H*), 8.53 (s, 1H, NC*H*).

Synthesis of L[B(OPr)] (3). Procedure as for **1** with H$_2$L (0.75 g, 3.52 mmol) and tri-*n*-propyl borate (0.66 g, 3.52 mmol) (0.55 g, 56%): Mp 191−195 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.68−0.71 (t, 3H, CH$_2$CH_3), 1.37−1.42 (m, 2H, CH$_2$CH_2), 3.25−3.37 (m, 2H, OCH_2), 6.90 (m, 2H, Ph*H*), 7.10 (m, 2H, Ph*H*), 7.24 (m, 2H, Ph*H*), 7.55 (m, 2H, Ph*H*), 8.53 (s, 1H, NC*H*).

Synthesis of L[B(OBu^n)] (4). Procedure as for **1** with H$_2$L (0.74 g, 3.46 mmol) and tri-*n*-butyl borate (0.80 g, 3.46 mmol) (0.59 g, 58%): Mp 192−196 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.72−0.77 (t, 3H, CH$_2$CH_3), 1.11−1.17 (m, 2H, CH$_2$CH_2), 1.32−1.38 (m, 2H, CH$_2$CH_2), 3.30−3.39 (m, 2H, OCH_2), 6.90 (m, 2H, Ph*H*), 7.10 (m, 2H, Ph*H*), 7.24 (m, 2H, Ph*H*), 7.55 (m, 2H, Ph*H*), 8.52 (s, 1H, NC*H*).

Synthesis of L(Cl)[B(OMe)] (5). Procedure as for **1** with H$_2$L(Cl) (1.00 g, 4.04 mmol) and trimethyl borate (0.42 g, 4.04 mmol) (0.85 g, 73%): Mp 192−194 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.14 (s, 3H, OCH_3), 6.93 (m, 1H, Ph*H*), 7.13 (m, 1H, Ph*H*), 7.24 (m, 1H, Ph*H*), 7.36 (m, 1H, Ph*H*), 7.50−7.52 (m, 3H, Ph*H*), 8.54 (s, 1H, NC*H*).

Synthesis of L(Cl)[B(OEt)] (6). Procedure as for **1** with H$_2$L(Cl) (0.50 g, 2.02 mmol) and triethyl borate (0.30 g, 2.02 mmol) (0.36 g, 60%): Mp 175−180 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.00−1.03 (t, 3H, CH$_2$CH_3), 3.36−3.42 (m, 2H, OCH_2), 6.95 (m, 1H, Ph*H*), 7.14 (m, 1H, Ph*H*), 7.22 (m, 1H, Ph*H*), 7.35 (m, 1H, Ph*H*), 7.51−7.53 (m, 3H, Ph*H*), 8.47 (s, 1H, NC*H*).

Synthesis of L(Cl)[B(OPr)] (7). Procedure as for **1** with H$_2$L(Cl) (0.81 g, 3.24 mmol) and tri-*n*-propyl borate (0.61 g, 3.24 mmol) (0.65 g, 63%): Mp 179−181 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.68−0.71 (t, 3H, CH$_2$CH_3), 1.36−1.39 (m, 2H, CH$_2$CH_2), 3.21−3.33 (m, 2H, OCH_2), 6.93 (m, 1H, Ph*H*), 7.12 (m, 1H, Ph*H*), 7.21 (m, 1H, Ph*H*), 7.32 (m, 1H, Ph*H*), 7.51−7.53 (m, 3H, Ph*H*), 8.47 (s, 1H, NC*H*).

Synthesis of L(Cl)[B(OBu^n)] (8). Procedure as for **1** with H$_2$L(Cl) (0.82 g, 3.31 mmol) and tri-*n*-butyl borate (0.76 g, 3.31 mmol) (0.65 g, 60%): Mp >260 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.75−0.78 (t, 3H, CH$_2$CH_3), 1.11−1.17 (m, 2H, CH$_2$CH_2), 1.32−1.37 (m, 2H, CH$_2$CH_2), 3.30−3.42 (m, 2H, OCH_2), 6.96 (m, 1H, Ph*H*), 7.11 (m, 1H, Ph*H*), 7.20 (m, 1H, Ph*H*), 7.33 (m, 1H, Ph*H*), 7.50−7.52 (m, 3H, Ph*H*), 8.47 (s, 1H, NC*H*).

Synthesis of L(Br)[B(OMe)] (9). Procedure as for **1** with H$_2$L(Br) (1.00 g, 3.42 mmol) and trimethyl borate (0.35 g, 3.42 mmol) (0.88 g, 78%): Mp 177−179 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.11 (s, 3H,

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OCH_3), 6.93 (m, 1H, PhH), 7.12 (m, 1H, PhH), 7.31 (m, 1H, PhH), 7.47 (m, 1H, PhH), 7.62−7.66 (m, 3H, PhH), 8.48 (s, 1H, NCH).

Synthesis of L(Br)[B(OEt)] (10). Procedure as for **1** with H$_2$L(Br) (0.50 g, 1.71 mmol) and triethyl borate (0.18 g, 1.71 mmol) (0.37 g, 63%): Mp 155−159 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.00−1.02 (t, 3H, CH$_2$CH_3), 3.35−3.44 (m, 2H, OCH_2), 6.92 (m, 1H, PhH), 7.13 (m, 1H, PhH), 7.29 (m, 1H, PhH), 7.41 (m, 1H, PhH), 7.62−7.66 (m, 3H, PhH), 8.46 (s, 1H, NCH).

Synthesis of L(Br)[B(OPr)] (11). To a stirred toluene/thf (4:1) solution (25 mL) of H$_2$L(Br) (0.50 g, 1.71 mmol) was added tri-*n*-propyl borate (0.32 g, 1.71 mmol) (0.51 g, 84%): Mp 183−184 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.65−0.69 (t, 3H, CH$_2$CH_3), 1.33−1.38 (m, 2H, CH$_2$CH_2), 3.21−3.34 (m, 2H, OCH_2), 6.90 (m, 1H, PhH), 7.11 (m, 1H, PhH), 7.23 (m, 1H, PhH), 7.44 (m, 1H, PhH), 7.63−7.68 (m, 3H, PhH), 8.45 (s, 1H, NCH).

Synthesis of L(Br)[B(OBu^n)] (12). Procedure as for **1** with H$_2$L(Br) (0.41 g, 1.40 mmol) and tri-*n*-butyl borate (0.32 g, 1.40 mmol) (0.34 g, 65%): Mp >260 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.75−0.78 (t, 3H, CH$_2$CH_3), 1.11−1.17 (m, 2H, CH$_2$CH_2), 1.32−1.37 (m, 2H, CH$_2$CH_2), 3.26−3.37 (m, 2H, OCH_2), 6.92 (m, 1H, PhH), 7.11 (m, 1H, PhH), 7.34 (m, 1H, PhH), 7.45 (m, 1H, PhH), 7.62−7.65 (m, 3H, PhH), 8.46 (s, 1H, NCH).

Synthesis of L[B(OSiPh$_3$)] (13). To a stirred toluene solution (25 mL) of L[B(OMe)] (0.52 g, 2.05 mmol) was added triphenylsilanol (0.57 g, 2.05 mmol). The resulting solution was refluxed for 3 h. Removal of solvent under vacuum followed by recrystallization from CH$_2$Cl$_2$ solution yielded orange crystals at −30 °C (0.42 g, 41%): Mp 215−218 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.80 (m, 1H, PhH), 6.91 (m, 1H, PhH), 6.97 (m, 1H, PhH), 7.05 (m, 1H, PhH), 7.18−7.37 (m, 15H, PhH), 7.22 (m, 1H, PhH), 7.33 (m, 1H, PhH), 7.49 (m, 1H, PhH), 7.63 (m, 1H, PhH), 8.12 (s, 1H, NCH); ^{11}B NMR (270 MHz, CDCl$_3$, external standard BF$_3$·Et$_2$O) δ 2.77.

Synthesis of L(Br)[B(OSiPh$_3$)] (14). To a stirred toluene solution (25 mL) of L(Br)[B(OBu^n)] (1.30 g, 3.48 mmol) was added triphenylsilanol (0.96 g, 3.48 mmol). The resulting solution was refluxed for 3 h. Removal of solvent under vacuum followed by recrystallization from CH$_2$Cl$_2$ solution provided a yellow solid at −30 °C (0.75 g, 38%): Mp 153−156 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.88 (m, 3H, PhH), 7.19−7.38 (m, 17H, PhH), 7.42 (m, 1H, PhH), 7.62 (m, 1H, PhH), 8.07 (s, 1H, NCH).

Synthesis of L[B(OTf)] (15). To solution of L[B(OMe)] (1.00 g, 3.95 mmol) in toluene (45 mL) was added a solution of trifluoromethanesulfonic acid (0.59 g, 3.95 mmol) in toluene (10 mL) at room temperature. The exothermic reaction produced a yellow precipitate. After being stirred overnight, the mixture was filtered and then recrystallized from thf to give a yellow solid (0.53 g, 35%): Mp 184−185 °C; ^{1}H NMR (270 MHz, DMSO) δ 1.75, 3.58 (t, m, 5H, thf) 6.98−7.85 (m, 8H, PhH), 9.30 (s, 1H, NCH); ^{11}B NMR (270 MHz, CDCl$_3$, external standard BF$_3$·Et$_2$O) δ 3.91.

Polymerization of Propylene Oxide with L[B(OTf)] (15). Method A. To L[B(OTf)] (0.51 g, 1.37 mmol) was added PO (30 mL, 422 mmol) via syringe. The mixture was stirred for 1 week at room temperature, and the unreacted monomer was removed under reduced pressure resulting in a viscous yellow oil. This was dissolved in CH$_2$Cl$_2$ (50 mL) and washed with 0.1 M HCl (30 mL). The organic layer was dried with MgSO$_4$, and CH$_2$Cl$_2$ was removed under vacuum to yield a viscous yellow oil (1.2 g).^{1}H NMR (CDCl$_3$): 1.11 (m), 3.42 (m). GPC: $M_w = 607$; $M_n = 416$; PDI = 1.46.

Method B. The similar procedure to that outlined above was employed at 8 psi by heating to 40 °C for 48 h to yield a yellow oil (2.0 g). ^{1}H NMR (CDCl$_3$): 1.15 (m), 3.50 (m). GPC: $M_w = 624$; $M_n = 414$; PDI = 1.51.

Polymerization of Propylene Oxide with [^{n}Bu$_2$B]OTf (16). Method A was used with **16** (3 mL of 1 M solution in CH$_2$Cl$_2$, 3.00 mmol) and PO (30 mL, 422 mmol) with stirring for 72 h to obtain a dark green oil (4.9 g). ^{1}H NMR (270 MHz, CDCl$_3$): 1.08 (m), 3.46 (m). GPC: $M_w = 1299$; no. average $M_n = 808$; PDI = 1.61.

Attempted Polymerization of PO with L[B(OMe)]. To L[B(OMe)] (0.50 g, 1.98 mmol) was added PO (30 mL, 422 mmol) via syringe. The resulting yellow solution was stirred for 48 h at 8 psi by heating to 40 °C. The excess monomer was removed under reduced pressure resulting in a yellow solid identified as unreacted starting material by ^{1}H NMR. This procedure was also attempted with L[B(OSiPh$_3$)].

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Supporting Information Available: Text providing infrared data and elemental analyses for compounds **1**−**15** (4 pages). Ordering information is given on any current masthead page. Crystallographic data (excluding the structure factor tables) for **13** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 10063. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, 44 (1223) 336-033; e-mail, teched@chemcrys.cam.ac.uk).

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